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(54) Title: CATALYST COMPRISING A BUFFERED IONIC LIQUID AND HYDROCARBON CONVERSION PROCESS, E.G. OLIGOMERISATION					
(57) Abstract					
<p>This invention relates to a buffered ionic liquid comprising: (A) a compound of the formula <math>R_nMX_{3-n}</math> or of the formula <math>R_mM_2X_{6-m}</math> wherein M is a metal selected from aluminium, gallium, boron and iron (III) R is a <math>C_1-C_6</math> alkyl radical, X is a halogen atom or an alkoxy group in which the alkyl group of said alkoxy group having 1-4 carbon atoms, n is 0, 1 or 2 and m is 1, 2 or 3; (B) an organic halide salt; and optionally, (C) an organic base wherein the relative mole-fractions of (A), (B) and (C) in the ionic liquid is within the ranges of 0.50-0.67 : 0.33-0.50 : 0.0-0.20. The ionic liquids can be used as a solvent or activator for hydrocarbon conversion catalyst such as e.g. during the oligomerisation of olefins with a nickel complex as catalyst.</p>					

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CATALYST COMPRISING A BUFFERED IONIC LIQUID AND HYDROCARBON CONVERSION PROCESS, E.G.  
OLIGOMERISATION

This invention relates to a novel catalyst composition comprising ionic liquids and the use thereof in a process such as eg the oligomerisation (including dimerisation) of olefins to linear products in a heterogeneous catalytic process.

The dimerization and oligomerisation of olefins in the presence of

5 homogeneous, Group VIII transition metal catalysts has been studied extensively. With higher olefins ( $>C_2$ ), the products obtained generally consist of mixtures of predominantly branched isomers. For example, gasoline blending components are produced by dimerization and codimerization of propylene and butenes. Bogdanovic et al (*Ind. Eng. Chem.*, **62** (12), 1970, pp. 34) have shown that for the catalyst system  $\pi$ -allyl-nickel halide/ $AlCl_3$ , the addition of bulky phosphanes gives rise to highly branched products.

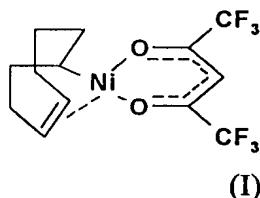
Very few catalysts are known which catalyse the dimerisation and oligomerisation of higher olefins to linear products. The dimerisation and

15 oligomerisation of  $C_3$ - $C_5$ - olefins to linear products is especially and highly desirable for the production of  $C_6$ - $C_{18}$  plasticisers and detergent range olefins. The major outlet for  $C_4$ -dimers is e.g. the conversion thereof, after

20 hydroformylation and hydrogenation, to plasticiser alcohols. Such plasticiser-alcohols made from linear dimers have higher thermal stabilities due to their relatively higher boiling points. Moreover, such linear dimers are preferred for use in the production of detergent-alkylates due to ease of their biological degradability.

Hitherto, the best known catalyst system for the homogeneous, linear dimerization of higher ( $>C_2$ ) olefins is that described by Keim et al. (*J. Mol. Cat.*, **6**, 1979, pp. 79) in which a square planar  $Ni-O, O'$ -chelating systems with

an easily replaceable group such as cyclo-octadienyl, methallyl-, allyl etc. such as e.g.:



5 which is Ni-cyclooctadienyl hexafluoroacetyl acetonate, is used. Table 1 shows the catalytic results of Keim et al when using (I) as a homogeneous catalyst in the dimerization of different olefins:

Table 1

10

Olefin	Activity/ 1/h	Selectivity (%) to dimers	Linearity (%) of dimers
ethylene	8200	20	100
propene	800	60	75
1-butene	500	85	75
1-hexene	300	90	60
1 octene	50	100	82

Although these results are very interesting especially for the dimerization of 1-butene, the high costs of the hexafluoroacetylacetone-ligand used, the relatively low activity of the catalyst and the amount of catalyst lost due to the homogenous nature of the process has rendered the process commercially unattractive.

15 To overcome these problems much work has been directed towards the use of heterogeneous catalysis. S. Gruppe (*Dissertation RWTH Aachen*, 1988) tried to anchor the NiO-catalyst (I) on a polymer backbone; A. Mehlhorn (*Dissertation RWTH Aachen*, 1991) investigated the introduction of the above mentioned NiO-catalyst (I) into zeolites. These strategies, however, resulted in considerable loss of catalyst due to leaching and hence resulted in much lower catalyst activity.

20 Ionic liquids are primarily mixtures of salts which melt below room temperature. Such salt mixtures include aluminium halides in combination with one or more of imidazolium halides, pyridinium halides and phosphonium halides, the latter being preferably substituted eg by alkyl groups. Examples of the substituted

derivatives of the latter include one or more of 1-methyl-3-butyl imidazolium halide, 1-butyl pyridinium halide and tetrabutyl phosphonium halides. Ionic liquids have been known as a solvent/activator for dimerization catalysts (eg nickel-phosphine catalysts). Conventional ionic liquid catalysts comprise about 67% 5 aluminium trichloride. However, these catalysts give rise to highly branched dimers (eg C<sub>6</sub> hydrocarbons) which are used as high RON/MON octane additives.

Ionic liquids are described as Lewis Acid catalysts for Friedel-Crafts reactions in prior published WO 95/21806 and olefin oligomerisation catalysts in prior published WO 95/21871. These ionic liquids consist of a mixture where the 10 mole ratio of AlX<sub>3</sub>/RX (in which X represents an alkyl group, a halide or a combination thereof, and R is an alkyl group) is usually > 1.5. When such ionic liquids are used for the oligomerisation of isobutene, a product having an average molecular weight of M = 1000 is obtained. In general, these acidic ionic liquids rapidly catalyse unselective oligomerisation of higher olefins to form highly viscous 15 and highly branched oligomers with the product having a broad molecular weight distribution (ie a high dispersity index). The use of such acidic ionic liquids without modification can lead to the formation of very low dimer selectivities (usually < 5 %). At room temperature and above, even with a Ni-catalyst, the main products are usually highly viscous cationic oligomers.

20 Chauvin et al. describe in a series of publications (*J. Chem. Soc., Chem. Commun.*, 1990, pp. 1715; *Ind. Eng. Chem. Res.*, 34, 1995, pp. 1149; and *J. Cat.*, 165, 1997, pp. 275) the preferred formation of dimers by the oligomerisation of higher olefins using slightly acidic ionic liquid of the type RX/AlX<sub>3</sub>/AlRCl<sub>2</sub> and a Ni-catalyst. However, at very low temperatures (usually -15°C), they describe the 25 formation of dimers from propene and butenes which are highly branched. Only at very low temperatures [usually -15 °C] or by addition of aluminiumalkyl halides such as AlEtCl<sub>2</sub> (ie ethyl aluminium dichloride) are improved dimer selectivities possible.

30 However, the addition of such aluminiumalkyl halides leads even at very low temperatures to the formation of highly branched dimers (usually < 10 % n-octenes for the dimerisation of 1-butene). This may be due to the tendency of AlEtCl<sub>2</sub> to transfer ethyl groups to the nickel thereby destroying the Ni-X,Y-chelating system, which is known to promote high linearity in the dimer. Another problem is that AlEtCl<sub>2</sub> is known to have strong isomerisation activity (Chauvin et al, *Angew. Chem.*, 107, 1995, pp. 2941) and converts the 1-butene rapidly into the 35

thermodynamically equilibrium distribution of butenes (around 4 % 1-butene at room-temperature).

5 A further alternative for the heterogenisation of NiO-catalyst (I) is to carry out the process in a two phase system. However, all of the common polar solvents such as eg water, butanediol etc used hitherto deactivate the catalyst system almost completely.

10 It has now been found that use of a modified ionic liquid as a solvent for the above described chelated complex of nickel such as eg Ni-cyclooctadienyl hexafluoroacetyl acetonate catalyst (I), a di(acetyl acetonate) of nickel or an analogue of either wherein the chelating ligand is a benzoyl trifluoroacetonato group ie  $\eta$ -4-cycloocten-1-yl)(benzoyl-trifluoroacetonato)nickel or a di(acetyl acetonato) group such as in eg nickel di(acetylacetonate) [hereafter Ni(acac)<sub>2</sub>] produces highly linear dimeric and oligomeric products.

15 Accordingly, the present invention is a buffered ionic liquid comprising:  
 20 A. a compound of the formula  $R_nMX_{3-n}$  or of the formula  $R_mM_2X_{6-m}$  wherein M is a metal selected from aluminium, gallium, boron and iron (III), R is a C<sub>1</sub>-C<sub>6</sub> alkyl radical, X is a halogen atom or an alkoxy group in which the alkyl group of said alkoxy group having 1-4 carbon atoms, n is 0, 1 or 2, and m is 1, 2 or 3  
 25 B. an organic halide salt; and optionally,  
 C. an organic base

characterised in that the relative mole-fractions of A, B and C in the ionic liquid is within the ranges 0.50-0.67 : 0.33-0.50 : 0.0-0.20.

30 In the ionic liquids of the present invention, the metal component M of compound A is aluminium, gallium, boron or iron (III) and is preferably aluminium. Where M is aluminium, compound A may be an aluminium halide or an alkyl aluminium halide such as an alkyl aluminium dichloride or dialuminium triethyl trichloride and is preferably ethyl aluminium dichloride. Where X is an alkoxy group compound A may be for instance dialkyl aluminium alkoxide, especially diethyl aluminium ethoxide ie  $(C_2H_5)_2Al(OC_2H_5)$ .

35 The organic halide salt (B) in the ionic liquid is suitably:  
 i. a hydrocarbyl substituted ammonium halide such as eg a mono-, di- or tri-alkyl ammonium halide represented by the generic formula  $R^4NR^1R^2R^3Cl$  wherein each of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> may be H or a C1-C8 alkyl groups, or

- ii. a hydrocarbyl substituted imidazolium halide or
- iii. a hydrocarbyl substituted pyridinium halide.

Especially preferred are the 1-alkyl-3-alkyl-imidazolium halides, the 1-alkyl pyridinium halides and the alkylene pyridinium dihalides. Specific examples of 5 these compounds include the following: 1-methyl-3-ethyl imidazolium chloride, 1-ethyl-3-butyl imidazolium chloride, 1-methyl-3-butyl imidazolium chloride, 1-methyl-3-butyl imidazolium bromide, 1-methyl-3-propyl imidazolium chloride, ethyl pyridinium chloride, ethyl pyridinium bromide, ethylene pyridinium dibromide, ethylene pyridinium dichloride, 4-methyl pyridinium chloride, butyl 10 pyridinium chloride and benzyl pyridinium bromide. Of these 1-methyl-3-ethyl imidazolium chloride and 1-methyl-3-butyl imidazolium chloride are preferred.

The organic base (C) is an optional ingredient. The catalyst will perform adequately even in the absence of a base in the sense that it will still produce a higher proportion of the linear dimers/oligomers if used in conjunction with an 15 ionic liquid solvent than when using toluene as the solvent. The base (C), when used, is suitably such that it has a relatively high solubility in the ionic liquid.

Examples of bases that may be used include *inter alia* any cyclic, heterocyclic or aliphatic, aromatic or non aromatic bases which have these properties. The bases used are preferably the pyrroles, pyridines, quinolines and their derivatives, 20 especially their hydrocarbyl substituted or halo-substituted derivatives wherein the hydrocarbyl substituents may be alkyl, aryl, alkaryl, aralkyl or cycloalkyl groups and the halo substituents are eg chloro, bromo or fluoro derivatives, especially the difluoro derivatives such as eg 2,6-difluoro-pyridine.

The buffered ionic liquid comprises (A), (B) and (C) in mole fraction 25 within the ranges of 0.50-0.67 : 0.33-0.50 : 0.0-0.20 respectively, suitably in the ranges from 0.50-0.57 : 0.45-0.50 : 0.001-0.05 respectively. A typical buffered ionic liquid preferably comprises (A), (B) and (C) in the mole-fraction ratio of 0.53 : 0.47 : 0.04 respectively.

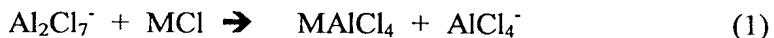
Ionic liquids of the present invention can be used as a solvent/activator for 30 catalysts, especially for catalysts such as the nickel compound (I) used in hydrocarbon conversion reactions such as eg dimerisation or oligomerisation. Where the ionic liquids are used in conjunction with a catalytic species such as eg the nickel compound (I) described above, the modification of the conventional ionic liquids by use of buffers minimises the tendency of the ionic liquid to promote 35 any undesirable side-reactions thereby adversely affecting the selectivity towards

the desired linear dimer.

The modified ionic liquid has to satisfy the following criteria:

- a. it has to be substantially free of any coordinating species such as e.g  $\text{Cl}^-$  (present e.g in basic chloroaluminate-based ionic liquids) which are capable of occupying the active sites in the catalyst;
- 5 b. it should have a slightly latent Lewis-acidity in the melt to allow activation of the catalyst and the substrate is extremely favourable for the reaction.
- c. at the same time the presence of any excess of free chloroaluminate-dimer should be avoided to minimise cationic side-reactions through a Lewis
- 10 Acid-base reaction with the olefin.
- d. it is easier to prepare and uses only relatively inexpensive material thereby improving the economics of the process.

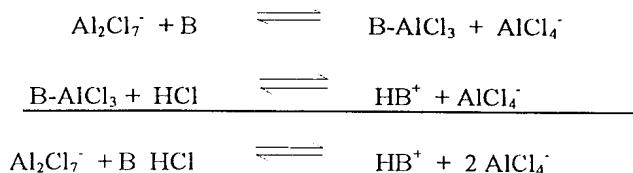
For this reason a used chloroaluminate-based ionic liquids has to be slightly acidic in nature but buffered to a certain amount of latent acidity which would enable it to avoid side reactions initiated by the ionic liquid itself without deactivation and destruction of (I): A number of reactions are described in the literature to buffer Lewis-Acid ionic liquids effectively to neutral ionic liquids with latent acidity (see D. King et al, *J.Am. Chem Soc.*, **118**, 1996, pp. 11933):



20 wherein M = Li, Na or K

Additionally, an alternative way to buffer the Lewis acidity of common acidic Lewis-acid ionic liquids to latent acidity is as follows:

The slightly acidic ionic liquids (having molar ratio of  $\text{AlCl}_3$  in the binary melt of usually of 53-55 %) by the addition thereto of a weak, system adapted, 25 non-coordinating base. The base reacts with any species in the melt which are capable of initiating any undesirable side reactions of the type shown below:



wherein B represents the base.

30 The choice of the base may enable variations in the selectivity of the catalyst to the desired products. A slightly acidic chloroaluminate system buffered down with 2,6-difluoropyridines shows eg a stronger selectivity to the trimerisation product

5 during the oligomerisation of 1-butene. The use of 2,6-difluoro-pyridine, for instance favours the formation of linear trimers from the mono-olefin. Thus, the choice of base may direct the reaction towards trimer formation in preference to dimers. Similarly, where the catalyst is a Ni(acac)<sub>2</sub>, it is advantageous to use such a catalyst together with an activator such as eg ethyl aluminium dichloride ("EADC") in order to improve the selectivity of the catalyst for a particular owner. In this case, the total amount of EADC and component A present in the formulation is slightly higher than when used in the absence of an activator. The additional amount of EADC used suitably corresponds to the stoichiometric 10 amount corresponding to the Ni(acac)<sub>2</sub> used. It is to be noted that if too much EADC is used, there is a risk of forming the higher, relatively less desirable, oligomers. It is not necessary to pre-form a Ni(acac)<sub>2</sub>-EADC system prior to use thereof as a catalyst in the ionic liquid. Thus, when using a Ni(acac)<sub>2</sub> catalyst system, this may be prepared in several ways. For instance, the Ni(acac)<sub>2</sub> may be 15 dissolved first in an ionic liquid comprising eg 55% AlCl<sub>3</sub>, followed by addition of the buffering base, if used, and finally adding a stoichiometric amount of EADC based on the Ni(acac)<sub>2</sub> used to this mixture. The resultant product can be used directly as a catalyst for the oligomerisation reaction. Alternatively, the EADC may first be added to the ionic liquid and then to this mixture Ni(acac)<sub>2</sub> can be 20 added to form the catalyst.

25 The buffering procedure enables activation of the NiO-catalyst (I) or the Ni(acac)<sub>2</sub> catalyst, or, an analogue of either in such modified ionic liquid solvents so as to maintain the selectivity thereof to the linear products, while suppressing substantially any undesirable cationic oligomerisation even at relatively high temperatures (eg up to 80°C).

30 The activity of the catalyst in two-phase reactions can in some instances be adversely affected by the viscosity of the phase, especially in respect of mixing and transfer phenomena in the system. In such cases, the adverse effect can be mitigated by addition of small amounts (eg < 20 vol % of the ionic liquid phase) of polar cosolvents such as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, fluorobenzene etc. to improve dramatically the physical properties of the ionic liquid. Such an expedient can increase the turn-over frequency of catalytic reaction up to four times without adversely affecting the desired selectivities. Only very small amounts (eg < 2 %) of the cosolvents are likely be lost in the organic layer comprising the feedstock and 35 dimerised products.

Thus, according to a further embodiment, the present invention relates to a hydrocarbon conversion catalyst wherein said catalyst is used as a solution thereof in or activated by a buffered ionic liquid according to the present invention as hereinbefore described.

5 The hydrocarbon conversion catalyst is suitably a co-ordination complex of nickel and is preferably ( $\eta$ -4-cycloocten-1-yl)-(benzoyl-trifluoroacetonato) nickel or nickel di(acetyl acetonate) or an analogue of either.

10 The hydrocarbon conversion catalyst according to the present invention is suitably used for the dimerisation or oligomerisation of unsaturated hydrocarbons, suitably olefins having from 2-20 carbon atoms, preferably olefins having 2-10 carbon atoms.

15 Thus, according to yet another embodiment, the present invention is a hydrocarbon converion process comprising the dimerisation or oligomerisation of unsaturated hydrocarbons characterised in that said process is carried out in the presence of a catalyst which is dissolved in or activated by a buffered ionic liquid of the present invention as hereinabove described.

The catalyst for dimerisation or oligomerisation is suitably a co-ordination complex of nickel as described above, preferably ( $\eta$ -4-cycloocten-1-yl)-(benzoyl-trifluoroacetonato) nickel or nickel di(acetyl acetonate), or, an analogue of either.

20 **Example 1: Use of pyrrole as the buffering base**

A 30 ml glass pressure vessel connected with a manometer and a stop cock was charged with N-methyl-N-butylpyridiniumchloride-AlCl<sub>3</sub> (4g, 24.3 mmol, 55% mol AlCl<sub>3</sub>). Pyrrole (0.072g, 1.08 mmol) was added to the charge in the vessel and stirred for 1 h. to form a solution of a buffered ionic liquid. The composition of the ionic liquid so formed was 4-methyl-N-butylpyridiniumchloride/AlCl<sub>3</sub>/pyrrole corresponding to 0.53/0.43/0.04 mole-fractions of each respectively. Ni-hexafluoro-acetylacetone (0.04g, 0.10mmol) catalyst was added to the ionic liquid and stirred for 15 min. when all the Ni-catalyst dissolved in the ionic liquid. The Ni-catalyst loading with respect to the ionic liquid was 14 mg/ml. The vessel was then cooled to -30°C and 20 ml of 1-butene (equivalent to 12 g, 0.21 mol) was charged to the vessel. The temperature of the vessel was then allowed to rise to 25°C.

35 The contents of the vessel were stirred with a stirrer at about 500 rpm and a reaction exotherm was observed over the first 5 minutes of the reaction, which was indicated by a pressure increase up to 4 bar. After another ten minutes (total

15 minutes), the stirring and consequently the reaction was stopped and the vessel was cooled down to 0°C. The vessel was then opened and the organic layer in the reaction mixture was decanted off. The organic layer was then stirred at room temperature for 2 hours to remove any traces of butenes. A short centrifugation of 5 the organic layer at 2000 turns/min was carried out to separate small drops of the ionic liquid from the organic layer. Measurements of residual Al and Ni in the organic layer after the reaction gave values of <1 ppm for each which provided evidence of efficient catalyst separation via gravity alone following reaction. The organic layer (mass 2g) was then recovered and analysed by GC and the following 10 results (compound/mass%) were obtained:

Traces of butenes	0.5 %
Σ of all C <sub>8</sub> -oligomers:	86.0 %
Σ higher oligomers	13.5 %
Total	100 %

15 Distribution of the C<sub>8</sub>-oligomers:

Σ n-Octenes	56 % comprising
n-octene-1	1.70 %
trans-octene-2	23.43 %
cis-octene-2	5.20 %
20 trans-octene-3	18.79 %
cis-octene-3	2.20 %
trans-octene-4	3.94 %
cis-octene-4	0.74 %
Σ Methylheptene	42 %
25 Σ Dimethylhexene	2 %
Total :	100 %

The above data correspond to the following :

Butene conversion:	16.7 %
Sel.(C8 product)	86.0 %
30 Sel.(linear C8 product)	56.0 %
Turn-over frequency 1/h	1350

Example 2: Use of quinoline as buffering base:

A 30 ml glass pressure-vessel connected with a manometer and a stop-cock 35 was charged with N-methyl-N-butylpyridiniumchloride-AlCl<sub>3</sub> (4g, 24.3 mmol, 55%

mol AlCl<sub>3</sub>). Then quinoline (0.139g, 1.08 mmol) was added to the charge in the vessel and stirred for 1 h. to form a solution of a buffered ionic liquid. The composition of the ionic liquid so formed was 4-methyl-N-butylpyridiniumchloride/AlCl<sub>3</sub>/quinoline corresponding to 0.53/0.43/0.04 mole-fractions of each respectively. Ni-hexafluoro-acetylacetone (0.04g, 0.10mmol) catalyst was added to the ionic liquid and stirred for 15 min. when all the Ni-catalyst dissolved in the ionic liquid. The Ni-catalyst loading with respect to the buffered ionic liquid was 14 mg/ml. The vessel was then cooled to -30°C and 20 ml of 1-butene (equivalent to 12 g, 0.21 mol) were charged to the vessel. The temperature of the vessel was then allowed to rise to 25°C.

The contents of the vessel were then stirred with a stirrer at about 500 rpm and a reaction exotherm was observed over the first 5 minutes of the reaction, which was indicated by pressure increase of up to 4 bar. After another ten minutes (total 15 minutes), the stirring and consequently the reaction was stopped and the vessel was cooled down to 0°C. The vessel was then opened and the organic layer in the reaction mixture was decanted off. The organic layer was then stirred at room temperature for 2 hours to remove any traces of butenes. A short centrifugation of the organic layer at 2000 turns/min was carried out to separate small drops of the ionic liquid from the organic layer.

Measurements of residual Al and Ni in the organic layer after the reaction gave values of <1 ppm for each which provided evidence of efficient catalyst separation via gravity alone following reaction. The organic layer (mass 1.8g) was then recovered and analysed by GC and the following results (compound/mass%) were obtained:

25	Traces of butenes	0.1 %
	Σ of all C <sub>8</sub> -oligomers:	98.0 %
	Σ higher oligomers	1.9 %
	Total	100 %

Distribution of the C<sub>8</sub>-oligomers:

30	Σ n-Octenes	64 % comprising
	n-octene-1	1.96%
	trans-octene-2	26.79 %
	cis-octene-2	5.89%
	trans-octene-3	21.48 %
35	cis-octene-3	2.49 %

	trans-octene-4	4.50 %
	cis-octene-4	0.86 %
	$\Sigma$ Methylheptene	34 %
	$\Sigma$ Dimethylhexene	2 %
5	Total :	100 %

The above data correspond to the following :

	Butene conversion:	15.0 %
	Sel. (C8 product)	98.0 %
	Sel (linear C8 product)	64.0 %
10	Turn-over frequency 1/h	1240

**Example 3: Use of 2,6-Lutidine (2,6-Dimethylpyridine) as buffering base:**

A 30 ml glass pressure vessel connected with a manometer and a stop-cock was charged with N-methyl-N-butylpyridiniumchloride-AlCl<sub>3</sub> (4.0g, 24.3 mmol, 55% mol AlCl<sub>3</sub>). Then 2,6-lutidine (0.116g, 1.08 mmol) was added to the charge in 15 the vessel and stirred for 1 h. to form a buffered ionic liquid. The composition of the ionic liquid so formed was 4-methyl-N-butylpyridiniumchloride/AlCl<sub>3</sub>/2,6-lutidine corresponding to 0.53/0.43/0.04 mole-fractions of each respectively. Ni-hexafluoro-acetylacetone (0.04g, 0.10mmol) catalyst was added to the ionic liquid and stirred for 15 min. when all the Ni-catalyst dissolved in the ionic liquid. 20 The Ni-catalyst loading with respect to the ionic liquid was 14 mg/ml. The vessel was then cooled to -30°C and 20 ml of 1-butene (equivalent to 12 g, 0.21 mol) was charged to the vessel. The temperature of the vessel was then allowed to rise to 25°C.

The contents of the vessel were stirred with a stirrer at about 500 rpm and 25 a reaction exotherm was observed over the first 5 minutes of the reaction, which was indicated by a pressure increase up to 4 bar. After another five minutes (total 10 minutes), the stirring and consequently the reaction was stopped and the vessel was cooled down to 0°C. The vessel was then opened and the organic layer in the reaction mixture was decanted off. The organic layer was then stirred at room 30 temperature for 2 hours to remove any traces of butenes. A short centrifugation of the organic layer at 2000 turns/min was carried out to separate small drops of the ionic liquid from the organic layer. Measurements of residual Al and Ni in the organic layer after the reaction gave values of <1 ppm of each which provided evidence of efficient catalyst separation via gravity alone following reaction. The 35 organic layer (mass 2.4g) was then recovered and analysed by GC and the

following results (compound/mass%) were obtained:

Traces of butenes	0.5 %
$\Sigma$ of all C <sub>8</sub> -oligomers:	55.0 %
$\Sigma$ higher oligomers	44.5 %
5 Total	100 %

Distribution of the C<sub>8</sub>-oligomers:

$\Sigma$ n-Octenes	68 % comprising
n-octene-1	2.08 %
trans-octene-2	28.42 %
10 cis-octene-2	6.28 %
trans-octene-3	38.08 %
cis-octene-3	2.65 %
trans-octene-4	4.76 %
cis-octene-4	0.89 %
15 $\Sigma$ Methylheptene	29 %
$\Sigma$ Dimethylhexene	3 %
Total :	100 %

The above data correspond to the following :

Butene conversion:	20.0 %
20 Sel.(C8 product)	55.0 %
Sel.(linear C8 product)	68.0 %
Turn-over frequency 1/h	2480

Example 4: Use of N-Methylpyrrole as buffering base

A 30 ml glass pressure-vessel connected with a manometer and a stop-cock was charged with N-methyl-N-butylpyridiniumchloride-AlCl<sub>3</sub> (3.5g, 22.4 mmol, 55% mol AlCl<sub>3</sub>) and cooled to -30 °C. Then 20 ml of 1-butene (equivalent to 12 g, 0.21 mol) were added. The catalyst was prepared by dissolving Ni-hexafluoro-acetylacetone (0.12g, 0.31 mmol) in 2 ml of N-methylpyrrole. Next, 0.08 mg of this catalyst solution were added rapidly into the vessel at -30 °C to give a yellow organic layer. The vessel temperature was allowed to rise to 25 °C.

The contents of the vessel were then stirred by a stirrer at about 500 rpm and very quickly, during the first 20 seconds, the organic layer became colourless and the ionic liquid changed its colour to a dark orange-brown. At this stage no N-methyl pyrrole could be found in the organic layer so that its composition was 4-methyl-N-butylpyridiniumchloride/AlCl<sub>3</sub>/ N-methyl pyrrole corresponding to

0.53/0.43/0.04 mole fractions of each respectively. The Ni-catalyst loading with respect to ionic liquid was thus 2mg/ml.

The contents of the vessel were stirred with a stirrer operating at 500 rpm and a reaction exotherm was observed over the first 5 minutes of the reaction,

5 which was indicated by pressure increase of up to 4 bar. After a further 10 minutes (total 15 minutes) the stirring and consequently the reaction was stopped and the reaction vessel cooled down to 0°C. The cooled vessel was then opened and the organic layer from the contents thereof was decanted off. The decanted organic layer was then stirred at room temperature for 2 hours to remove any traces of

10 butenes. A short centrifugation of the organic layer at 2000 turns/min was carried out to separate small drops of the ionic liquid out of the organic layer.

Measurements of residual Al and Ni in the organic layer after reaction gave values of <1 ppm for each which provided evidence of efficient catalyst separation via gravity alone following reaction. The organic layer (mass 1.8g) was then recovered

15 and analysed by GC and the following results (compound/mass %) were obtained:

Traces of butenes:	0.2 %
Σ of all C <sub>8</sub> -oligomers:	98.0 %
Σ higher oligomers:	1.8 %
Total	100 %

20 Distribution of the C<sub>8</sub>-oligomers:

Σ n-Octenes	56 %
n-octene-1	1.70 %
trans-octene-2	23.43 %
cis-octene-2	5.20 %
25 trans-octene-3	18.79 %
cis-octene-3	2.20 %
trans-octene-4	3.94 %
cis-octene-4	0.74 %
Σ Methylheptene	42 %
30 Σ Dimethylhexene	2 %
Total :	100 %

The above data correspond to the following :

Butene conversion: 15 %

Sel. (C<sub>8</sub> product) 98 %

35 Sel (linear C<sub>8</sub> product) 55 %

Turnover frequency 1/h 9920

**Example 5: Use of (h-4-Cycloocten-1-yl)(benzoyl-trifluoroacetonato) nickel as catalyst:**

A 30 ml glass pressure-vessel connected with a manometer and a stop-cock  
5 was charged with N-methyl-N-butylpyridiniumchloride-AlCl<sub>3</sub> (4g, 24.3 mmol, 55% mol AlCl<sub>3</sub>). Then pyrrole (0.072g, 1.08 mmol) was added to the charge in the vessel and stirred for 1 h. to form a solution of a buffered ionic liquid. The composition of the ionic liquid so formed was 4-methyl-N-butylpyridiniumchloride/AlCl<sub>3</sub>/pyrrole corresponding to 0.53/0.43/0.04 mole-fractions respectively. 0.04g  
10 (0.1mmol) of (h-4-cycloocten-1-yl)-(benzoyl-trifluoroacetonato) nickel was added to the ionic liquid and stirred for 5 min. when all the Ni-catalyst dissolved in the ionic liquid. The Ni-catalyst loading with respect to ionic liquid was thus 14 mg/ml. The vessel was then cooled to -30 °C and 20 ml of 1-butene (equivalent to 12 g, 0.21 mol) were charged to the vessel. The temperature of the vessel was allowed  
15 to rise to 25°C.

The contents of the vessel were then stirred by a stirrer operating at about 500 rpm and a reaction exotherm was observed over the first 5 minutes of the reaction, which was indicated by pressure increase up to 4 bar. After a further 10 minutes (total 15 minutes), the stirrer and consequently the reaction was stopped  
20 and the vessel was cooled down to 0°C. The vessel was opened and the organic layer of the contents thereof was decanted off. The organic layer was then stirred at room temperature for 2 hours to remove any traces of butenes. A short centrifugation of the organic layer at 2000 turns/min was carried out to separate small drops of the ionic liquid out of  
25 the organic layer. Measurements of residual Al and Ni in the organic layer after reaction gave values of <1 ppm for each which provided evidence of efficient catalyst separation via gravity alone following reaction. The organic layer (mass 0.65g) was then recovered and analysed by GC and the following results (compound/mass%) were obtained:

30 Traces of butenes: 0.1 %  
Σ of all C<sub>8</sub>-oligomers: 55.0 %  
Σ higher oligomers: 44.9  
Total 100 %  
35 Distribution of the C<sub>8</sub>-oligomers:  
Σ n-Octenes 66 %

	n-octene-1	1.98 %
	trans-octene-2	27.59 %
	cis-octene-2	6.08 %
	trans-octene-3	22.16 %
5	cis-octene-3	2.57 %
	trans-octene-4	4.62 %
	cis-octene-4	0.87 %
	$\Sigma$ Methylheptene	31%
	$\Sigma$ Dimethylhexene	3 %
10	Total :	100 %

The above data correspond to the following :

	Butene conversion:	5.4 %
	Sel. (C8 product)	55 %
	Sel (linear C8 product)	66 %
15	Turnover frequency 1/h	450

**Example 6: Influence of methylene chloride**

A 30 ml glass pressure vessel connected with a manometer and a stop-cock was charged with N-methyl-N-butylpyridiniumchloride-AlCl<sub>3</sub> (5g, 31.3 mmol, 55% mol AlCl<sub>3</sub>). Then pyrrole (0.072g, 1.08 mmol) were added to the charge in the vessel and stirred for 1 h. to form a buffered ionic liquid. The composition of the ionic liquid so formed was 4-Methyl-N-butylpyridiniumchloride/ AlCl<sub>3</sub>/pyrrole equal to 0.53/0.43/0.04 mole fractions of each respectively. 0.04g (0.1mmol) of (h-4-cycloocten-1-yl)-(benzoyl-trifluoroacetonato) nickel were added to the ionic liquid and stirred for 5 min. when all the Ni-catalyst dissolved in the ionic liquid. 25 The Ni-catalyst loading with respect to the buffered ionic liquid was thus 14 mg/ml. At this stage 1 ml of methylene chloride was added to the buffered ionic liquid and the resulting solution stirred for another 3 min. The vessel was then cooled to -30°C and 20 ml of 1-butene (equivalent to 12 g, 0.21 mol) were charged to the vessel. The temperature of the vessel was allowed to rise to 25°C.

30 The reaction mixture in the vessel was stirred by a stirrer operated at about 500 rpm and a reaction exotherm was observed over the first 5 minutes of the reaction, which was indicated by pressure increase of up to 4 bar. After a further 10 minutes (total 15 minutes), the stirring and consequently the reaction was stopped and the vessel was cooled down to 0°C. The vessel was opened and the 35 organic layer was decanted off. The organic layer was then stirred at room

temperature for 2 hours to remove any traces of butenes. A short centrifugation of the organic layer at 2000 turns/min was carried out to separate small drops of the ionic liquid out of the organic layer. Measurements of residual Al and Ni in the organic layer after reaction gave values of <1 ppm for each which provided 5 evidence of efficient catalyst separation via gravity alone. The organic layer (2.4g) was then analysed by GC and the following results (compound/mass%) were obtained:

Traces of butenes:	0.1 %
Methylenchloride	0.05 %
Σ of all C <sub>8</sub> -oligomers:	52.0 %
Σ higher oligomers:	47.85 %
Total	100 %

Distribution of the C<sub>8</sub>-oligomers:

Σ n-Octenes	64 %
15 n-octene-1	1.96 %
trans-octene-2	26.79 %
cis-octene-2	5.89 %
trans-octene-3	21.48 %
cis-octene-3	2.49 %
20 trans-octene-4	4.50 %
cis-octene-4	0.86 %
Σ Methylheptene	33 %
Σ Dimethylhexene	3 %
Total :	100 %

25 The above data correspond to the following :

Butene conversion:	20 %
Sel. (C8 product)	98 %
Sel (linear C8 product)	64 %
Turnover frequency 1/h	1680

30 Example 7: Use of Pyrrole as the buffering base at 60°C

A 30 ml glass pressure-vessel connected with a manometer and a stop-cock was charged with N-methyl-N-butylpyridiniumchloride-AlCl<sub>3</sub> (4 g, 24.3 mmol, 5% mol AlCl<sub>3</sub>). Then pyrrole (0.072 g, 1.08 mmol) was added to charge in the vessel and stirred for 1 h to form a solution of a buffered ionic liquid. The composition of 35 the ionic liquid so formed was 4-methyl-N-butylpyridiniumchloride/AlCl<sub>3</sub>/pyrrole

corresponding to 0.53/0.43/0.04 mole-fractions of each respectively. 0.04g (0.10 mmol) Ni-hexafluoroacetyl-acetonate were added to the ionic liquid and stirred for 15 min. when all the Ni-catalyst dissolved in the ionic liquid. The Ni-catalyst loading with respect to the ionic liquid was thus 14 mg/ml. The vessel was then 5 cooled to

-30°C and 20 ml of 1-butene (equiv to 12 g, 0.21 mol) were condensed in. The vessel was heated to 60°C.

The contents of the vessel were stirred with a stirrer operating at 500 rpm and a reaction exotherm was observed over the first 5 mins of the reaction, which 10 was indicated by a pressure increase of up to 8 bar. After a further 10 minutes (total 15 minutes), the stirring and consequently the reaction was stopped and the vessel was cooled down to 0°C. The vessel was then opened and the organic layer in the reaction mixture was decanted off. The organic layer was then stirred at room temperature for 2 hours to remove any traces of butenes. A short 15 centrifugation of the organic layer at 2000 turns/min was carried out to separate small drops of the ionic liquid out of the organic layer. Measurements of residual Al and Ni in the organic layer after reaction gave values of <1 ppm for each which provided evidence of efficient catalyst separation via gravity alone following reaction. The organic layer (mass 2.1 g) was then recovered and analysed by GC 20 and the following results (compound/mass%) were obtained:

Traces of butenes	0.5 %
$\Sigma$ of all C <sub>8</sub> -oligomers:	86.0 %
$\Sigma$ higher oligomers	13.5 %
Total	100 %

25 Distribution of the C<sub>8</sub>-oligomers:

$\Sigma$ n-Octenes	56 %
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n-octene-1
trans-octene-2
cis-octene-2
30 trans-octene-3
cis-octene-3
trans-octene-4
cis-octene-4

$\Sigma$ Methylheptene	42 %
35 $\Sigma$ Dimethylhexene	2 %

Total : 100 %

The above data correspond to the following:

Butene conversion: 17.5 %

Sel. (C8 product) 86.0 %

5 Sel. (linear C8 product) 56.0 %

Turnover frequency 1/h 1450

Example 8: ( $\eta$ -4-Cycloocten-1-yl)(benzoyl-trifluoroacetonato)nickel at 60°C

A 30 ml glass pressure-vessel connected with a manometer and a stop-cock was charged with N-methyl-N-butylpyridiniumchloride-AlCl<sub>3</sub> (4 g, 24.3 mmol,

10 55% mol AlCl<sub>3</sub>). Then pyrrole (0.072 g, 1.08 mmol) was added to the charge in the vessel and stirred for 1 h. to form a buffered ionic liquid. The composition of the ionic liquid was 4-methyl-N-butylpyridiniumchloride/AlCl<sub>3</sub>/pyrrole corresponding to 0.53/0.43/0.04 mole-fractions of each respectively. 0.04g (0.1mmol) of ( $\eta$ -4-cycloocten-1-yl)-(benzoyl-trifluoroacetonato) nickel was added to the ionic liquid

15 and stirred for 5 minutes when all the Ni-catalyst dissolved in the ionic liquid. The Ni-catalyst loading with respect to the ionic liquid was thus 14 mg/ml. The vessel was then cooled to -30°C and 20 ml of 1-butene (equiv to 12 g, 0.21 mol) were

condensed in. The vessel was heated to 60°C.

The contents of the vessel were stirred with a stirrer operating at 500 rpm and a reaction exotherm was observed over the first 5 mins of the reaction, which was indicated by a pressure increase of up to 8 bar. After a further 10 minutes

(total 15 minutes), the stirring and consequently the reaction was stopped and the vessel cooled down to 0°C. The vessel was then opened and the organic layer in the reaction mixture was decanted off. The organic layer was then stirred at room temperature for 2 hours to remove any traces of butenes. A short centrifugation of the organic layer at 2000 turns/min was carried out to separate small drops of the ionic liquid out of the organic layer. Measurements of residual Al and Ni in the

25 organic layer after reaction gave values of <1 ppm for each which provided evidence of efficient catalyst separation via gravity alone following reaction. The organic layer (mass 0.7 g) was then recovered and analysed by GC and the following results (compound/mass%) were obtained:

Traces of butenes: 0.1 %

$\Sigma$  of all C<sub>8</sub>-oligomers: 55.0 %

$\Sigma$  higher oligomers: 44.9

35 Total 100 %

Distribution of the C<sub>8</sub>-oligomers:

	$\Sigma$ n-Octenes	66 %
	n-octene-1	
	trans-octene-2	
5	cis-octene-2	
	trans-octene-3	
	cis-octene-3	
	trans-octene-4	
	cis-octene-4	
10	$\Sigma$ Methylheptene	31%
	$\Sigma$ Dimethylhexene	3 %
	Total :	100 %

The above data correspond to the following :

	Butene conversion:	5.8 %
15	Sel. (C8 product)	55 %
	Sel. (linear C8 product)	66 %
	Turnover frequency 1/h	500

Comparative Test 1: 1-Butene as catalyst solvent (not according to the invention)

20 A 30 ml glass pressure-vessel connected with a manometer and a stop-cock was charged with Ni-hexafluoroacetylacetone (0.04g (0.10 mmol). The vessel was then cooled to -30°C and 20 ml of 1-butene (equiv to 12 g, 0.21 mol) were condensed in. The temperature of the vessel was allowed to rise to 25°C.

25 The contents of the vessel were stirred with a stirrer operating at 500 rpm and no reaction exotherm was observed over a reaction time of 15 mins. The stirring and consequently the reaction was stopped and the vessel cooled down to 0°C. The vessel was then opened and the organic layer in the reaction mixture was then stirred at room temperature for 2 hours to remove any traces of butenes. No organic product was obtained.

30 mass of the organic layer was: 0g

Comparative Test 2: Toluene as catalyst solvent (not according to the invention)

A 30 ml glass pressure-vessel connected with a manometer and a stop-cock was loaded with 4 g toluene. 0.04g (0.10 mmol) Ni-hexafluoroacetylacetone were added and stirred for 3 min. when all the Ni-catalyst dissolved in toluene. The

vessel was then cooled to -30°C and 20 ml of 1-butene (equiv to 12 g, 0.21 mol) were condensed in. The temperature of the vessel was allowed to rise to 25°C.

5 The contents of the vessel were then stirred with a stirrer operating at 500 rpm and no reaction exotherm was observed over a reaction time of 15 minutes. The stirring and consequently the reaction was stopped and the vessel cooled down to 0°C. The vessel was then opened and the organic layer in the reaction mixture was then stirred at room temperature for 2 hours to remove any traces of butenes. The organic layer (4g) was then recovered and analysed by GC and the following results (compound/mass%) were obtained:

10	Traces of butenes	0.45 %
	Toluene	99.5 %
	$\Sigma$ of all C <sub>8</sub> -oligomers:	0.05 %
	Total	100 %

**Example 9**

15 A stoichiometric ratio of Ni(acac)<sub>2</sub> catalyst to EADC activator was dissolved in an ionic liquid (IL) of formula 2-methylbutylpyridinium chloride-aluminium chloride (55 % mol AlCl<sub>3</sub>), the ratio of (catalyst+activator) to IL being 1:150 mol/mol. 1-butene feedstock was added such that the ratio of IL:feed was 150:1400 mol/mol. This mixture was stirred in a batch autoclave at 23°C for 15 mins at 600 rev/min.

20 N-methylpyrrole was added in some cases to the ionic liquid in order to minimise side reactions of olefin feedstock to higher oligomers. Table 1 below shows the effect of the level of free base addition on catalyst performance where TOF represents turnover frequency, ie moles of product over number of active nickel atom sites:

25

Table 1

wt% N-methylpyrrole	TOF/ second	Selectivity (C <sub>8</sub> ) %	Linearity (C <sub>8</sub> ) %
2	320	45	75
3	600	68	48
4	700	98	50
6	900	98	40

Table 1 shows that the Ni(acac)<sub>2</sub> catalyst can also produce C<sub>8</sub> dimer, without the presence of fluorinated side groups. In addition, the data show that the addition of

free base is beneficial to catalyst performance, in terms of activity, selectivity to dimer and dimer linearity.

The Ni(acac)<sub>2</sub> catalyst system is much easier to handle and is much cheaper than the fluorinated catalysts. When used in combination with a free base, it is possible to obtain linear dimer product with equivalent activity, selectivity and linearity as with fluorinated catalyst.

**Example 10**

A mixture of 4-methylbutylpyridinium chloride-AlCl<sub>3</sub> ionic liquid (IL) and N-methylpyrrole in the ratio of 96:4 mol/mol was used to solvate Ni(acac)<sub>2</sub>:ETAC catalyst and raffinate 2 feedstock (butanes 25.7%, 2-butenes 58.8%, 1-butene 11.3%, iso-butene < 5% w/w) added to the mixture, in the ratio IL/catalyst/feedstock = 1/150/1400 mol/mol. Stirring was maintained at 600 revs/min and temperature of 50°C for 60 mins. Table 2 below shows the results :

15

Table 2

TOF/hr	Selectivity (C <sub>8</sub> dimer)%	Linearity (C <sub>8</sub> ) %
149	71	11

The data highlight the poor catalyst activity (turnover) and low linearity of dimer product when using raffinate 2 as feedstock instead of 1-butene. This is believed to be due to the difficulty of dimerising 2-butene to linear product, with 2-butene being present at levels of 58.8 % w/w in the raffinate 2 feedstock.

**Example 11**

By mixing Ni hexafluoroacetylacetone catalyst, ionic liquid (IL) buffered with 2,6-difluorolutidine (96:4 IL:base mol), and 1-butene feedstock in the ratio catalyst:IL:feed = 1:150:1400 at 600 revs/min at 23°C for 15 mins in batch autoclave mode, the catalyst behaviour was modified such that it was now selective to C<sub>12</sub> trimer rather than C<sub>8</sub> dimer. The results of this experiment are shown in Table 3 below:

Table 3

TOF/hr	Selectivity (C <sub>8</sub> dimer)%	Selectivity (C <sub>12</sub> trimer) %	Linearity (C <sub>8</sub> ) %	Linearity (C <sub>12</sub> ) %
730	29	50	72	10

## Claims:

1. A buffered ionic liquid comprising:
  - A. a compound of the formula  $R_nMX_{3-n}$  or of the formula  $R_mM_2X_{6-m}$  wherein M is a metal selected from aluminium, gallium, boron and iron (III) R is a C<sub>1</sub>-C<sub>6</sub> alkyl radical, X is a halogen atom or an alkoxy group in which the alkyl group of said alkoxy group having 1-4 carbon atoms, n is 0, 1 or 2, and m is 1, 2 or 3
  - B. an organic halide salt; and optionally,
  - C. an organic basecharacterised in that the relative mole-fractions of (A), (B) and (C) in the ionic liquid is within the ranges 0.50-0.67 : 0.33-0.50 : 0.0-0.20.
- 10 2. A buffered ionic liquid according to Claim 1 wherein the metal component M of compound (A) is aluminium, gallium, boron or iron (III).
3. A buffered ionic liquid according to Claim 2 wherein M is aluminium and compound (A) is an aluminium halide or an alkyl aluminium halide or a dialuminium trialkyl trihalide or a dialkylaluminium alkoxide.
- 15 4. A buffered ionic liquid according to Claim 3 wherein compound (A) is ethyl aluminium dichloride, dialuminium triethyl trichloride or diethyl aluminium ethoxide  $[(C_2H_5)_2Al(OC_2H_5)]$ .
5. A buffered ionic liquid according to any one of the preceding Claims wherein the organic halide salt (B) in the ionic liquid is :
  - 20 i. a hydrocarbyl substituted ammonium halide such as eg a mono-, di- or tri-alkyl ammonium halide represented by the generic formula  $R^4NR^1R^2R^3Cl$  wherein each of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> may be H or a C1-C8 alkyl groups, or
  - ii. a hydrocarbyl substituted imidazolium halide or
  - 25 iii. a hydrocarbyl substituted pyridinium halide.

6. A buffered ionic liquid according to Claim 5 wherein the organic halide salt (B) is selected from 1-alkyl-3-alkyl-imidazolium halides, the 1-alkyl pyridinium halides and the alkylene pyridinium dihalides.
7. A buffered ionic liquid according to Claim 6 wherein the organic halide salt (B) is selected from the group consisting of 1-methyl-3-ethyl imidazolium chloride, 1-ethyl-3-butyl imidazolium chloride, 1-methyl-3-butyl imidazolium chloride, 1-methyl-3-butyl imidazolium bromide, 1-methyl-3-propyl imidazolium chloride, ethyl pyridinium chloride, ethyl pyridinium bromide, ethylene pyridinium dibromide, ethylene pyridinium dichloride, 4-methyl pyridinium chloride, butyl pyridinium chloride and benzyl pyridinium bromide.
8. A buffered ionic liquid according to any one of the preceding Claims wherein the organic base (C) is such that it has a relatively high solubility in the ionic liquid.
9. A buffered ionic liquid according to any one of the preceding Claims wherein the organic base (C) is an open chain, cyclic or heterocyclic base which may be aliphatic, aromatic or non-aromatic.
10. A buffered ionic liquid according to any one of the preceding Claims wherein the organic base (C) is selected from a pyrrole, pyridine, quinoline and derivatives thereof.
11. A buffered ionic liquid according to Claim 10 wherein the derivatives of the organic base (C) are the hydrocarbyl substituted or halo-substituted derivatives in which the hydrocarbyl substituent is selected from alkyl, aryl, alkaryl, aralkyl or cycloalkyl groups and the halo substituent derivative is selected from chloro, bromo or fluoro derivatives.
12. A buffered ionic liquid according to Claim 10 or 11 wherein the organic base (C) is 2,6-difluoro-pyridine.
13. A buffered ionic liquid according to any one of the preceding Claims wherein said ionic liquid comprises (A), (B) and (C) in mole fraction ratios within the ranges of 0.50-0.57 : 0.45-0.50 : 0.001-0.05 respectively.
14. A buffered ionic liquid according to any one of the preceding Claims wherein said ionic liquid comprises (A), (B) and (C) in the mole-fraction ratio of 0.53 : 0.47 : 0.04 respectively.
15. A hydrocarbon conversion catalyst wherein said catalyst is used as a solution thereof in or activated by a buffered ionic liquid according to any one of the preceding Claims.

16. A hydrocarbon conversion catalyst according to Claim 15 wherein said catalyst is a co-ordination complex of nickel.
17. A hydrocarbon conversion catalyst according to Claim 15 or 16 wherein said catalyst is ( $\eta$ -4-cycloocten-1-yl)-(benzoyl-trifluoroacetonato) nickel or nickel di(acetyl acetonate), or, an analogue of either.  
5
18. A hydrocarbon conversion catalyst according to any one of the preceding Claims 15 to 17 wherein said catalyst is used for the dimerisation or oligomerisation of said hydrocarbon.
19. A hydrocarbon converion process comprising the dimerisation or 10 oligomerisation of unsaturated hydrocarbons characterised in that said process is carried out in the presence of a catalyst which is dissolved in or activated by a buffered ionic liquid according to any one of the preceding Claims 1-14.
20. A hydrocarbon conversion process according to Claim 19 wherein the catalyst is a co-ordination complex of nickel.
- 15 21. A hydrocarbon conversion process according to Claim 19 or 20 wherein the catalyst is ( $\eta$ -4-cycloocten-1-yl)-(benzoyl-trifluoroacetonato) nickel or nickel di(acetyl acetonate), or, an analogue of either.

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 98/00992

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 B01J31/30 C10G50/00

According to International Patent Classification(IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01J C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 550 304 A (CHAUVIN YVES ET AL) 27 August 1996 see claims; example 1 ---	1-7, 15-21
X	Y. CHAUVIN ET AL.: "Oligomerization of n-Butenes catalyzed by Ni Complexes dissolved in Organochloroaluminate Ionic Liquids" JOURNAL OF CATALYSIS, vol. 165, 1997, pages 275-278, XP002070945 cited in the application see the whole document ---	1-7, 15-21
X	WO 95 21872 A (BP CHEM INT LTD ; ABDUL SADA ALA A K (GB); SEDDON KENNETH RICHARD () 17 August 1995 see claims; table 1 ---	1-7, 15, 18, 19 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance  
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Date of the actual completion of the international search

Date of mailing of the international search report

9 July 1998

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 98/00992

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>RIECHL T L ET AL: "THE ELECTROCHEMISTRY OF ALUMINUM AND PROTONS IN ROOM TEMPERATURE CHLORO-ALUMINATE MOLTEN SALTS BUFFERED WITH SODIUM CHLORIDE" 1 January 1992, EXTENDED ABSTRACTS, VOL. 92/1, PAGE(S) 774/775 XP000549348 see column 1, paragraph 4</p> <p>---</p>	1-7
X	<p>BOON J A ET AL: "AN ELECTROCHEMICAL INVESTIGATION OF THE 1-METHYL-3-ETHYLIMIDAZOLIUM BROMIDE ALUMINUM BROMIDE MOLTEN SALT SYSTEM" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 138, no. 2, 1 February 1991, pages 465-469, XP000278362 see figure 1</p> <p>-----</p>	1-7

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No  
PCT/GB 98/00992

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